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# Probing the structure of a liquid metal during vitrification

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**Abstract**—Using aerodynamic levitation, vitrification of a ternary Zr–Cu–Al alloy was observed in-situ by high energy synchrotron radiation X-ray diffraction in the temperature range from above the liquidus $T_{liq}$ to well below the glass transition temperature $T_g$. The evolution of the atomic structure was studied using pair distribution functions (PDF) and molecular dynamic (MD) simulations. Vitrification was rendered possible due to the enhanced stability of the undercooled Zr–Cu melt after Al addition. Results indicate three regimes in the liquid alloy's structural pathway to vitrification. Short (SRO) and medium range order (MRO) develop significantly during cooling the liquid phase to the glassy state. The rate of structural rearrangements is enhanced in the super-cooled liquid between $T_{liq}$-140 K and $T_g$. The populations of atomic clusters with icosahedral local symmetry become predominant as $T_g$ is approached and facilitate vitrification and suppression of crystal nucleation and growth. The scenario of a possible fragile to strong transition in the super-cooled liquid is discussed.


*Keywords:* Metallic glasses; Vitrification; Atomic structure; Levitation; Synchrotron radiation

## 1. Introduction

Unlike crystalline structures that produce X-ray diffraction sharp peaks [1], in liquids the diffracted X-ray intensity is distributed as a succession of broad maxima from which the atomic structure cannot be directly obtained [2,3]. If the atomic structure of a liquid consists only of tetrahedra (or icosahedra of 20 tetrahedra), a barrier to crystallization will naturally occur [4] since tetrahedra cannot fill space with a periodic lattice (long-range-order). Prior to the emergence of computers, Bernal [5] approached the structure of mono-atomic liquids as a dense-random-packing (DRP) of hard spheres and discovered a set of nearly atomic-size canonical "holes" that filled the empty space in the DRP of tetrahedra. In fact, while a single icosahedron of 20 tetrahedra is the densest possible atomic packing for a cluster of that size, it can be shown that a mono-atomic DRP achieves a spatial packing fraction of about 66.4% as compared to 74% for periodic fcc or hcp atomic packing. This difference would roughly correspond to nearly one less nearest-neighbor (*nn*) in the liquid than in the crystalline state.

The ability of a liquid to undercool is related to the interfacial energy needed for nuclei of a crystalline phase to form [6]. Some metallic melts can be vitrified into a glassy state with no long-range order if they can be cooled through the undercooled liquid regime fast enough to suppress nucleation of crystalline phases [7]. The first eutectic alloys that were vitrified by splat-quenching at some $10^5$ K/s [8] were binary metals with about 20% metalloid elements such as $Au_{75}Si_{25}$, $Pd_{80}Si_{20}$ and $Fe_{80}B_{20}$. It was envisioned [9] that the smaller metalloid atoms occupied the canonical holes of Bernal-type DRP liquid structures, thus jamming the packing and reducing the atomic mobility needed for the construction of nuclei of a periodic lattice. Since the canonical holes in a DRP of hard spheres include centers of trigonal prisms, "capped trigonal prisms" which are a common motif of atomic chemical and topological short-range-order (SRO) in metal–metalloid crystalline intermetallics, were interconnected in various ways to define possible medium-range-order (MRO) in metalloid-containing vitrified alloys [10]. However, for the structure of subsequently discovered metalloid-free vitrified alloys such as $Cu_{60}Zr_{40}$, the solvent atoms were smaller than the solute atoms and could not be accommodated in the holes

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of a Bernal-type DRP assembly [11]. It has since been established that the structures of metallic glasses, which are mainly constituted of atomic species with attractive interactions, are packings of "efficiently packed clusters" rather than dense random packings of individual atoms, as explained in a topological model [12] and established by computer simulations and experiments [13–16]. In many cases, the constituent clusters that serve as atomic-level building blocks of metallic glasses are imperfect and interpenetrating icosahedra as recently demonstrated by direct observation using Angstrom beam electron diffraction [17,18].

The structure of a vitrifiable liquid alloy above $T_m$ is quite different from that of its glassy state with strong local atomic (cluster) ordering and the way that the former transforms into the latter during vitrification is generally unknown. Concerning diffraction studies, this limitation was related to the experimental acquisition times being longer or of the same order as the quenching time of the undercooled melt between $T_m$ and $T_g$. Recent advances in containerless techniques such as electrostatic and aerodynamic levitation gave new possibilities to study liquids and undercooled metallic melts using synchrotron and neutron scattering techniques [19–23]. However the acquisition of structural information in the whole temperature range from the liquid to the glassy state for metals remains challenging since avoiding crystallization during cooling requires cooling rates that are not easily achievable during in-situ diffraction experiments.

The teams of A. Inoue [24], W.L. Johnson [25] and more recently others have developed complex multi-component alloys that can be vitrified by slow cooling down from $T_m$, sometimes at only degrees per second. Cooling one such metal–metalloid alloy ($Pd_{40}Cu_{30}Ni_{10}P_{20}$) in a high energy synchrotron beam, we recently reported a full set of data tracing the path to vitrification from $T_{liq}$ to below $T_g$ [26,27]. Others have more recently reported such data for a quaternary ZrCuNiAl alloy [28].

Since diffraction experiments yield total atomic radial distribution functions (total pair distribution functions PDF) [29–31], it is important to reduce the number of components in order to better understand the evolution of the atomic structure during vitrification. Total PDFs are a convolution of contributions from atomic pair partial distribution functions which are unknown and evolve during vitrification with the evolution of chemical and topological order.

The transition of a liquid to a glass occurs with a remarkable slowdown of the dynamics in the undercooled liquid, a phenomenon which remains poorly understood. The dynamic arrest is manifested by an increase of viscosity by several orders of magnitude between the melting $T_m$ and the glass transition temperature $T_g$. The increase in viscosity for strong liquids follows an Arrhenius-type profile with temperature, whereas for fragile liquids it may strongly deviate from an Arrhenius behavior [32–34]. More recently a strong to fragile transition has been suggested for some liquids including metallic ones, pointing to a change from a non-Arrhenius behavior at high temperatures (above $T_m$) to an Arrhenius behavior as the liquid approaches the glass transition temperature ($T_g$) [35–39].

In the present work we report the results of in-the-beam vitrification of a ternary metalloid-free alloy ($Zr_{60}Cu_{30}Al_{10}$) at the European Synchrotron Radiation Facility using containerless levitation melting. Results show a drastic evolution of total atomic pair distribution function as atomic short-range order develops during vitrification. Application of computational methods (molecular dynamics simulation) to the experimental PDFs allows deconvolution of the total PDFs into partial pair distribution functions and shows how the hetero-atomic bonding in the undercooled liquid evolves. Results reveal high populations of a number of atomic cluster topologies, the temperature dependence of which indicates the predominance of icosahedra as $T_g$ is approached.

The experiment was rendered possible by the enhanced stability of the undercooled Zr–Cu melt after Al addition. Calculations using density functional theory were applied and confirmed that Al-addition results in strong covalent-like bonding in the liquid which then can be vitrified at lower cooling rates, allowing ample time to follow the vitrification process by diffraction methods.

## 2. Experimental details

Spherical ingots of about 2 mm diameter with composition $Zr_{60}Cu_{30}Al_{10}$ (% at, nominal composition) were prepared by arc melting the pure elements (purity 99.9 at.% or better) in an argon atmosphere using pure Ti as an oxygen getter. The ingots were remelted at least 5 times to achieve chemical homogeneity.

In-situ X-ray diffraction experiments were carried out at the ID-15 beamline of the European Synchrotron Radiation Facility (ESRF). The incident beam wavelength was 0.1245 Å (100 keV). Diffraction spectra were acquired in transmission mode by a 2D Perkin Elmer detector. An aerodynamic levitation setup [23] was used to melt and quench the metallic glass spheres. The spheres were levitating by high purity argon flow through an aluminum nozzle and melted using two $CO_2$ laser beams. Two pyrometers were used to record the temperature; temperature values below 620 K were calculated. Diffraction intensities were recorded during cooling with a time resolution of 100 ms as a function of the scattering vector Q (up to 25 $Å^{-1}$), where $Q = 4\pi \sin\theta/\lambda$, $\lambda$ is beam wavelength and $2\theta$ is the diffraction angle. The temperature readings were verified using the crystallization and melting temperatures of the alloys; the accuracy of the temperature values is estimated to be ±12 K above 900 K and better than ±7 K below 900 K.

The 2D diffraction images were azimuthally integrated after the necessary corrections for polarization and dark current using the FIT2D software [40]. The total structure factors $S(Q)$ and the reduced pair distribution functions $G(r)$ were obtained from the integrated diffraction intensities $I(Q)$ after corrections for sample absorption, Laue diffuse scattering, background contribution and normalization to the atomic X-ray form factor with the help of the PDFgetX3 software package [41]. The total structure factor $S(Q)$ yields the total coherent scattering intensity normalized by the incident flux per atom in the sample. The reduced pair distribution function, $G(r)$, was obtained from the sine-Fourier transform of the total structure factor $S(Q)$ [29].

$$G(r) = \frac{2}{\pi}\int_{Q_{\min}}^{\infty} Q[S(Q) - 1]\ sin\, QdQ \qquad (1)$$

In practice, the integral in the above Eq. (2) is limited to a maximum $Q = Q_{max}$. In this study a value of $Q_{max} = 16$ Å was used; higher $Q_{max}$ values were only found to increase